THEORY AND APPLICATION OF CONDUCTIVITY

BACKGROUND

Conductivity is a measure of how well a solution conducts electricity. To carry a current a solution must contain charged particles, or ions. Most conductivity measurements are made in aqueous solutions, and the ions responsible for the conductivity come from electrolytes dissolved in the water. Salts (like sodium chloride and magnesium sulfate), acids (like hydrochloric acid and acetic acid), and bases (like sodium hydroxide and ammonia) are all electrolytes. Although water itself is not an electrolyte, it does have a very small conductivity, implying that at least some ions are present. The ions are hydrogen and hydroxide, and they originate from the dissociation of molecular water. See Figure 1.
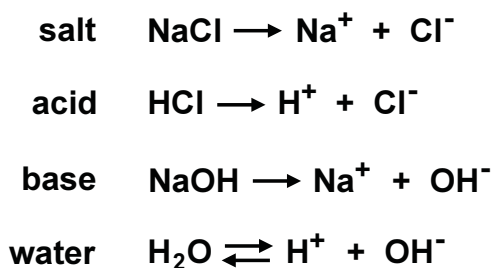
salt $\quad NaCl \longrightarrow Na^+ + Cl^-$

acid $\quad HCl \longrightarrow H^+ + Cl^-$

base $\quad NaOH \longrightarrow Na^+ + OH^-$

water $\quad H_2O \rightleftharpoons H^+ + OH^-$

FIGURE 1. Salts, acids, and bases are electrolytes. They dissolve in water to form ions. Although water is not an electrolyte, a very small concentration of hydrogen and hydroxide ions are always present in pure water.

Conductivity is not specific. It measures the total concentration of ions in solution. It cannot distinguish one electrolyte or ion from another.

Not all aqueous solutions have conductivity. Solutions of non-electrolytes, for example sugar or alcohol, have no conductivity because neither sugar nor alcohol contains ions nor do they produce ions when dissolved in water.

APPLICATIONS OF CONDUCTIVITY

Conductivity measurements are widely used in industry. Some important applications are described below.

• Water treatment. Raw water as it comes from a lake, river, or the tap is rarely suitable for industrial use. The water contains contaminants, largely ionic, that if not removed will cause scaling and corrosion in plant equipment, particularly in heat exchangers, cooling towers, and boilers. There are many ways to treat water, and different treatments have different goals. Often the goal is demineralization, which is the removal of all or nearly all of the contaminants. In other cases the goal is to remove only certain contaminants, for example hardness ions (calcium and magnesium). Because conductivity is a measure of the total concentration of ions, it is ideal for monitoring demineralizer performance. It is rarely suitable for measuring how well specific ionic contaminants are being removed.

Conductivity is also used to monitor the build up of dissolved ionic solids in evaporative cooling water systems and in boilers. When the conductivity gets too high, indicating a potentially harmful accumulation of solids, a quantity of water is drained out of the system and replaced with water having lower conductivity.

• Leak detection. Water used for cooling in heat exchangers and surface condensers usually contains large amounts of dissolved ionic solids. Leakage of the cooling water into the process liquid can result in potentially harmful contamination. Measuring conductivity in the outlet of a heat exchanger or in the condenser hotwell is an easy way of detecting leaks.
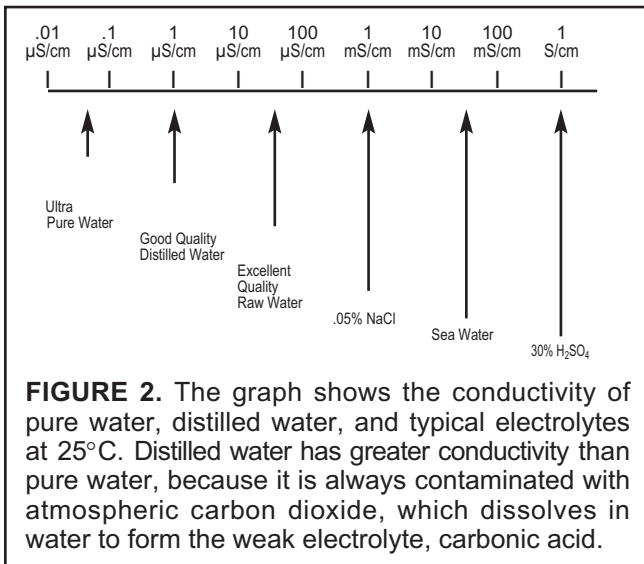
• Clean in place. In the pharmaceutical and food and beverage industries, piping and vessels are periodically cleaned and sanitized in a procedure called clean-in-place (CIP). Conductivity is used to monitor both the concentration of the CIP solution, typically sodium hydroxide, and the completeness of the rinse.

• Interface detection. If two liquids have appreciably different conductivity, a conductivity sensor can detect the interface between them. Interface detection is important in a variety of industries including chemical processing and food and beverage manufacturing.

• Desalination. Drinking water desalination plants, both thermal (evaporative) and membrane (reverse osmosis), make extensive use of conductivity to monitor how completely dissolved ionic solids are being removed from the brackish raw water.

UNITS

The units of conductivity are siemens per cm (S/cm). Derived units are µS/cm (one millionth of a S/cm) and mS/cm (one thousandth of a S/cm). S/cm is the same as the older unit mho/cm. Certain high purity water industries, primarily semiconductor and pharmaceutical, use resistivity instead of conductivity. Resistivity is the reciprocal of conductivity. The units are $M\Omega$ cm. Figure 2 shows the approximate conductivity of some typical electrolyte solutions.

| .01 µS/cm | .1 µS/cm | 1 µS/cm | 10 µS/cm | 100 µS/cm | 1 mS/cm | 10 mS/cm | 100 mS/cm | 1 S/cm |

Ultra Pure Water

Good Quality Distilled Water

Excellent Quality Raw Water

.05% NaCl

Sea Water

30% H_2SO_4

FIGURE 2. The graph shows the conductivity of pure water, distilled water, and typical electrolytes at 25°C. Distilled water has greater conductivity than pure water, because it is always contaminated with atmospheric carbon dioxide, which dissolves in water to form the weak electrolyte, carbonic acid.
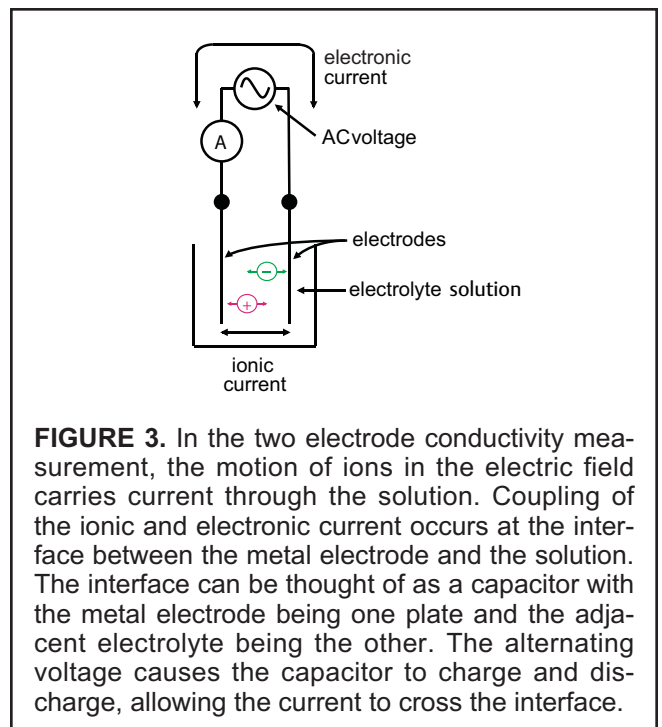
MEASUREMENT OF CONDUCTIVITY

There are two types of conductivity measurement: contacting and inductive. The choice of which to use depends on the amount of conductivity, the corrosiveness of the liquid, and the amount of suspended solids. Generally, the inductive method is better when the conductivity is high, the liquid is corrosive, or suspended solids are present.

Contacting Conductivity

Most contacting conductivity sensors consist of two metal electrodes, usually stainless steel or titanium, in contact with the electrolyte solution. See Figure 3. The analyzer applies an alternating voltage to the electrodes. The electric field causes the ions to move back and forth producing a current. Because the charge carriers are ions, the current is called an ionic current. The analyzer measures the current and uses Ohm's law to calculate the resistance of the solution (resistance = voltage/current). The conductance of the solution is the reciprocal of the resistance.

The ionic current depends on the total concentration of ions in solution and on the length and area of the solution through which the current flows. The current path is defined by the sensor geometry, or cell constant, which has units of 1/cm (length/area). Multiplying the conductance by the cell constant corrects for the effect of sensor geometry on the measurement. The result is the conductivity, which depends only on the concentration of ions.

electronic current

AC voltage

A

electrodes

electrolyte solution

$\ominus$

$\oplus$

ionic current

FIGURE 3. In the two electrode conductivity measurement, the motion of ions in the electric field carries current through the solution. Coupling of the ionic and electronic current occurs at the interface between the metal electrode and the solution. The interface can be thought of as a capacitor with the metal electrode being one plate and the adjacent electrolyte being the other. The alternating voltage causes the capacitor to charge and discharge, allowing the current to cross the interface.

Although the cell constant has a geometric interpretation (length divided by area), it is rarely calculated from dimensional measurements. In most designs the electric field is not confined between the electrodes, so the actual length and area are greater than predicted. In practice, the cell constant is measured against a solution of known conductivity. The cell constant is the ratio of the known conductivity (µS/cm) to the measured conductance (µS).

The usual conductivity range for a contacting sensor is 0.01 to 50,000 uS/cm. Because a given cell constant can be used only over a limited range, two, possibly three, cell constants are required to cover the entire range. Common cell constants are 0.01/cm, 0.10/cm, 1.0/cm, and 10/cm. Higher conductivity samples require larger cell constants.

Typically, the cell constant is measured at the factory, and the user enters the value in the analyzer when the sensor is first put in service. Cell constants change very little during the life of the sensor; however, the cell constant should be periodically checked, and the sensor recalibrated if necessary.

Some contacting sensors have four electrodes. See Figure 4. In the four electrode measurement, the analyzer injects an alternating current through the outer electrodes and measures the voltage across the inner electrodes. The analyzer calculates the conductance of the electrolyte solution from the current and voltage. Because the voltage measuring circuit draws very little current, charge transfer effects at the metal-liquid interface are largely absent in four-electrode sensors. As a result, a single four-electrode sensor has a much wider dynamic range than a two-electrode sensor, roughly 1 to 1,4000,000 µS/cm. Like the two-electrode sensor, the four-electrode sensor has a cell constant, which depends on the area, spacing, and arrangement of the current and voltage electrodes. The cell constant
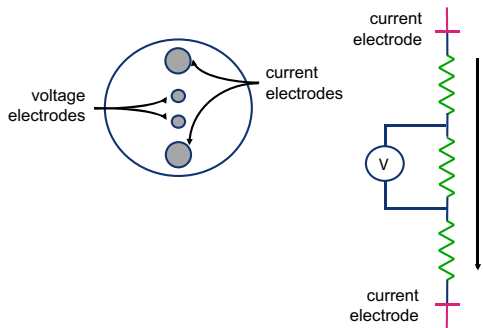
FIGURE 4. In the four electrode conductivity measurement, the analyzer injects current between the outer electrodes and measures the voltage drop caused by the resistance of the electrolyte between the inner electrodes.

is measured at the factory, and the user enters the value in the analyzer at startup.

Contacting conductivity measurements are restricted to applications where the conductivity is fairly low (although four-electrode sensors have a higher end operating range) and the sample is non-corrosive and free of suspended solids. Two-electrode sensors are ideal for measuring high purity water in semi-conductor, steam electric power, and pharmaceutical plants.

Inductive Conductivity

Inductive conductivity is sometimes called toroidal or electrodeless conductivity. An inductive sensor consists of two wire-wound metal toroids encased in a corrosion-resistant plastic body. One toroid is the drive coil, the other is the receive coil. The sensor is immersed in the conductive liquid. The analyzer applies an alternating voltage to the drive coil, which induces a voltage in the liquid surrounding the coil. The voltage causes an ionic current to flow proportional to the conductance of the liquid. The ionic current induces an electronic current in the receive coil, which the analyzer measures. The induced current is directly proportional to the conductance of the solution. See Figure 5.
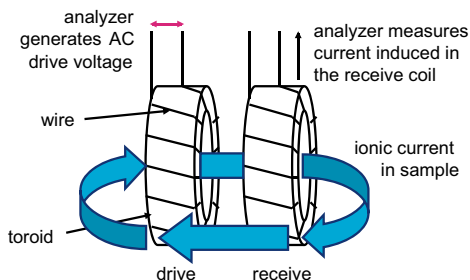

FIGURE 5. Both coils are encased in a single sensor body and overmolded with plastic. The coils must be completely submerged in the process liquid.

The current in the receive coil depends on the number of windings in the drive and receive coils and the physical dimensions of the sensor, which defines the volume of sample through which the ionic current flows. The number of windings and the dimensions of the sensor are described by the cell constant. As in the case of contacting sensors, the product of the cell constant and conductance is the conductivity.

The walls of the tank or pipe in which the sensor is installed also influence the cell constant—the so-called wall effect. A metal (conducting) wall near the sensor increases the induced current, leading to increased conductance and a corresponding decrease in the cell constant. A plastic or insulating wall has the opposite effect. Normally, wall effects disappear when the distance between the sensor and wall reaches roughly three-fourths of the diameter of the sensor. See Figure 6. Because some degree of wall effect is present in most installations, factory-determined cell constants are of little use. For accurate results, the user must calibrate the sensor in place in the process piping.

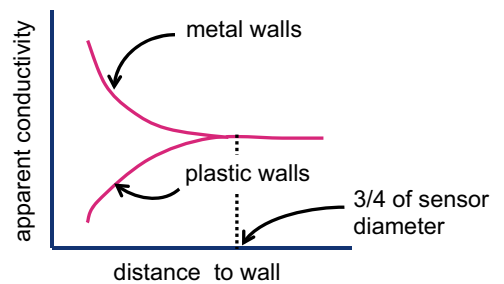The inductive measurement has several benefits.

FIGURE 6. For typical sensors, wall affects disappear when the clearance between the sensor and wall is 1 – 1 ½ in (25 – 37 mm).

First, the toroids do not need to touch the sample. Thus, they can be encased in plastic, allowing the sensor to be used in solutions that would corrode metal electrode sensors. Second, because inductive sensors tolerate high levels of fouling, they can be used in solutions containing high levels of suspended solids. As long as the fouling does not appreciably change the area of the toroid opening, readings will be accurate. By contrast, even a light coating of deposit on a contacting sensor will cause an error. Finally, inductive sensors are ideal for measuring solutions having high conductivity. High conductivity solutions produce a large, easily measured induced current in the receive coil.

Inductive sensors do have drawbacks. Chiefly, they are restricted to samples having conductivity greater than about 15 µS/cm. They cannot be used for measuring low conductivity solutions.

TEMPERATURE AND CONDUCTIVITY

Increasing the temperature of an electrolyte solution always increases the conductivity. The increase is significant, between 1.5 and 5.0% per °C. To compensate for temperature changes, conductivity readings are commonly corrected to the value at a reference temperature, typically 25°C. All process conductivity sensors have integral temperature sensors that allow the analyzer to measure the process temperature and correct the raw conductivity. Three temperature correction algorithms are in common use.

- Linear temperature coefficient
- High purity water or dilute sodium chloride
- Cation conductivity or dilute hydrochloric acid

No temperature correction is perfect. Unless the composition of the process liquid exactly matches the model used in the correction algorithm, there will be an error. In addition, errors in the temperature measurement itself will lead to errors in the corrected conductivity.

Linear temperature coefficient

The linear temperature correction is widely used. It is based on the observation that the conductivity of an electrolyte changes by about the same percentage for every °C change in temperature. The equation is

$$C_{25} = \frac{C_t}{1 + \alpha(t\text{-}25)}$$

C_{25} is the calculated conductivity at 25°C, C_t is the raw conductivity at t°C, and α is the linear temperature coefficient expressed as a decimal fraction. Although a single temperature coefficient can be used with reasonable accuracy over a range of 30° or 40°C, accuracy can be improved by calculating a coefficient specifically for the sample temperature. Approximate ranges for linear temperature coefficients are shown below:

acids	1.0 – 1.6 % per °C
bases	1.8 – 2.2 % per °C
salts	1.8 – 3.0 % per °C

High purity water

The high purity water correction assumes the sample is pure water contaminated with sodium chloride (NaCl). The measured conductivity is the sum of the conductivity from water and the conductivity from the sodium and chloride ions.

Figure 7 also shows how the high purity water correction works. Point 1 is the raw conductivity. The first step is to subtract the conductivity of pure water at the measurement temperature from the raw conductivity. The result is point 2, the conductivity of sodium and chloride. Next, the conductivity of sodium and chloride

is converted to the value at 25°C, point 3. Finally, the conductivity of pure water is added to the result to give the corrected conductivity at 25°C, point 4.
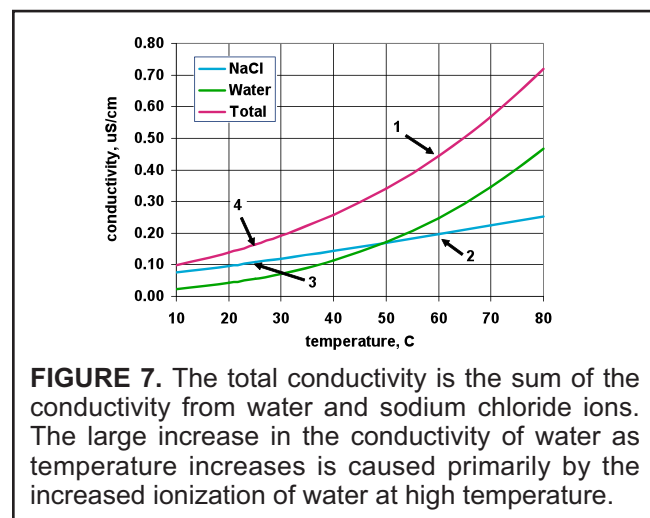

FIGURE 7. The total conductivity is the sum of the conductivity from water and sodium chloride ions. The large increase in the conductivity of water as temperature increases is caused primarily by the increased ionization of water at high temperature.

Cation conductivity

The cation conductivity temperature correction is unique to the steam electric power industry. Cation conductivity is a way of detecting ionic contamination in the presence of background conductivity caused by ammonia or neutralizing amines, which are added to the condensate and feedwater to elevate the pH and reduce corrosion. In cation conductivity, the amines are removed and the ionic contaminant is converted to the equivalent acid, for example sodium chloride is converted to hydrochloric acid.

The cation conductivity model assumes the sample is pure water contaminated with hydrochloric acid. The correction algorithm is more complicated than the high purity water correction because the contribution of water to the overall conductivity depends on the amount of acid present. Hydrochloric acid suppresses the dissociation of water, causing its contribution to the total conductivity to change as the concentration of hydrochloric acid changes.

CALIBRATION

There are two ways to calibrate conductivity sensors. The sensor can be calibrated against a solution of known conductivity or it can be calibrated against a previously calibrated sensor and analyzer. Normally, the sensor should be calibrated at a point near the midpoint of the operating range calibration changes the cell constant.

Calibration against a standard solution

Calibration against a standard solution is straightforward. Place the sensor in the standard and adjust the analyzer reading to match the known conductivity. To eliminate temperature related errors, disable temperature compensation and calibrate using the conductivity

of the standard at the measurement temperature. Most conductivity standards are solutions of potassium chloride, so even if temperature and conductivity data are not on the label, the data are readily available in reference books.

Conductivity standards are susceptible to contamination from atmospheric carbon dioxide. Carbon dioxide dissolves in water forming carbonic acid and increasing the conductivity by as much as 1.5 µS/cm. To minimize contamination errors, avoid using standards with conductivity less than about 150 µS/cm.

Calibration against a referee sensor and analyzer

The best way to calibrate a process sensor against a referee is let the process liquid flow through the sensors connected in series and adjust the process reading to match the referee analyzer. Turning off temperature compensation in both analyzers eliminates temperature compensation errors. To ensure the temperature is the same at both sensors, keep sample flow high and tubing runs short. Use clean interconnecting tubing to avoid contamination. Because the system is protected from atmospheric contamination, the method is ideal for calibrating sensors used to measure low conductivity samples.

An alternative procedure is to take a grab sample of the process liquid and measure its conductivity in the shop or laboratory. Because the sample temperature is likely to change during the measurement, temperature compensation is required. It is important that the temperature measurement in both the process and referee analyzers be accurate and that the temperature correction algorithms be identical. Grab sample calibration is, of course, unsuitable for samples having low conductivity.

MEASURING CONCENTRATION

Although conductivity is non-specific, if certain conditions are met, it can be used to measure the concentration of electrolyte solutions. Examples are measuring the concentration of CIP (clean in place) chemicals and measuring the concentration of acid and caustic solutions used to regenerate ion exchange demineralizers.

To infer concentration from conductivity several requirements must be met:

1. The liquid must contain a single electrolyte or the electrolyte of interest must be the major contributor to the conductivity. For example, when cation exchange resin is regenerated with sulfuric acid, the concentrated acid is diluted with service water to between 2 and 12% (90,000 to 490,000 µS/cm). The highest the service water conductivity is likely to be is 800 µS/cm, making the worst case error about 1%.

2. There must be a measurable change in conductivity over the concentration range, and the conductivity must be increasing or decreasing over the range.

Figure 8 shows a graph of conductivity versus concentration for a typical electrolyte and the range over which concentration can be inferred from conductivity. Not all curves have the maximum shown in the graph, but many do. Some electrolytes, for example, sulfuric acid, have curves with two maxima.

3. Sufficient data must be available to allow a temperature coefficient to be estimated. If the data are not available in reference books, they must be determined experimentally.
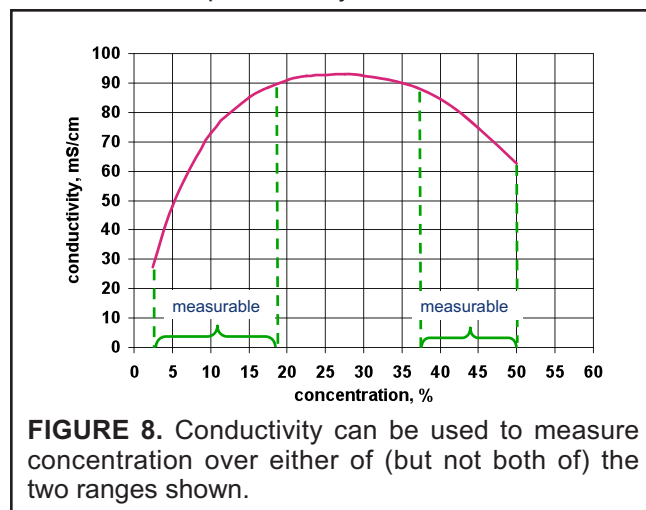

FIGURE 8. Conductivity can be used to measure concentration over either of (but not both of) the two ranges shown.

SENSORS, ANALYZERS, AND TRANSMITTERS

Rosemount Analytical offers contacting and inductive sensors, analyzers, and transmitters to meet most industrial needs and applications. For more information consult the product data sheets listed below and on the next page.

CONTACTING SENSORS (All two-electrode except 410VP)		
Model	Description	PDS
140	General purpose, retractable	71-140 series
141	General purpose, screw in	71-140 series
142	General purpose, screw in	71-140 series
400 and 400VP	General purpose, screw in	71-400
402 and 402VP	General purpose, retractable	71-400
403 and 403VP	Sanitary flange	71-403
404	Flow through	71-400
410VP	Four-electrode sanitary flange	71-410VP

INDUCTIVE (TOROIDAL) SENSORS		
Model	Description	PDS
225	Sanitary flange	71-225
226	General purpose, large toroid opening	71-226/228
228	General purpose, small toroid opening	71-226/228
222	Flow through w/bolted flange connections	71-222
242	Flow through w/bolted flange connections	71-242
245	Flow through with sanitary connections	71-245

ANALYZERS AND TRANSMITTERS		
Model	Description	PDS
1056	Four-wire, dual input, dual output	71-1056
54eC	Four-wire, single input, dual output	71-54e
Xmt-C and Xmt-T	Two-wire, single input, single output	71-Xmt
5081-C and 5081-T	Two-wire, single input, single output, explosion proof	71-5081

All Rosemount Analytical analyzers and transmitters are compatible with the sensors listed above, with the exception of the 410VP sensor, which is compatible only with the 1056. All instruments feature linear slope, high purity water, and cation temperature corrections. Built-in conductivity-concentration curves are available for sodium hydroxide, hydrochloric acid, sulfuric acid (two ranges), and sodium chloride (except 54eC). All analyzers have a custom curve feature that calculates a conductivity to concentration curve from user-entered data.

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